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FORMATION OF PORES IN GRANULATED MINERAL MATERIALS UNDER FIRING

A. N. Emel'yanov[1]

Based on the regularities of the growth of gas bubbles, crystallization of metals, and topochemical reactions of decomposition of solids, the kinetic equation of pore formation in granules of mineral materials under firing is derived. The obtained equations are recommended for mathematical modeling of the pore formation process in granulated foam glass and porous fillers.

One of the main physicochemical processes determining the formation of pores in pelletized mineral materials under firing is the growth of gas bubbles [1 – 4]. It is shown in [5, 6] that the behavior of a conglomeration of gas bubbles of size up to 2.5 mm is fully identical to the behavior of solid spherical particles of the same size. Therefore, in constructing a kinetic equation to describe pore formation in granules of natural argillaceous material with additives (organic, mineral, or complex organomineral additives) and glass powders of different chemical compositions, and in subsequent experimental verification, the equation describing the crystallization of metals was used. This equation was applied to determine the portion of material participating in the reactions $\alpha(\tau)$ depending on the process duration, and a method was proposed [7] for the calculation of the equation coefficients

$$\alpha(\tau) = 1 - \exp(-k\tau)^b, \tag{1}$$

where k and b are the process constants; τ is the process duration.

The kinetic equation of pore formation in granules at a constant temperature, corroborated by statistical processing of experimental data related to firing granules of various mineral materials, was derived on the basis of the following assumptions.

In the initial moment of firing ($\tau = 0$), a granule has the volume V_{min} and contains elementary gas bubbles (the pore seeds) with the average volume V_f each. The expansion (frothing or swelling) of a gas bubble occurs in the following way. Within a short time period, the bubble volume grows from V_f to V_r, but the moments of frothing or swelling of different gas bubbles occur at different times and randomly.

Let us assume that some of the elementary gas bubbles have expanded their volume by the time τ elapsed since the

[1] Samara State Architectural and Construction Academy, Samara, Russia.

start of the firing; then the volume of the swelled (frothed) part will be equal to $\alpha(\tau)(V_{min}/V_f)V_r$, and the volume of the remaining non-swelled part will be $[1 - \alpha(\tau)]V_{min}$. Hence the volume of the granule at the moment τ will be equal to:

$$V(\tau) = \alpha(\tau)\frac{V_{min}}{V_f} V_r + [1 - \alpha(\tau)]V_{min}.$$

Since $\alpha(\infty) = 1$ (all elementary gas bubbles in the granule are swelled)

$$V(\infty) = \frac{V_r}{V_f} V_{min}; \quad \frac{V_r}{V_f} = \frac{V(\infty)}{V_{min}}.$$

Therefore, one can write:

$$V(\tau) = \alpha(\tau)V(\infty) + [1 - \alpha(\tau)]V_{min}. \tag{2}$$

The basic assumption verified for various types of mineral materials (clay, glass, and ash-slag residue after burning of solid fuel) implies that $\alpha(\tau)$, i.e., the part of the initial granule volume that had swelled by the moment τ, satisfies equation (1), known as the Kolmogorov – Erofeev equation.

By substituting expression (1) in formula (2), we get:

$$V(\tau) = (1 - \exp(-k\tau)^b)V(\infty) + V_{min}\, e^{-k\tau^b}$$

or

$$\frac{V(\tau) - V(\infty)}{V_{min} - V(\infty)} = e^{-k\tau^b}. \tag{3}$$

Assuming that the granule weight at this firing temperature varies insignificantly, we finally obtain:

$$\frac{1/\rho(\tau) - 1/\rho_{min}}{1/\rho_{max} - 1/\rho_{min}} = e^{-k\tau^b}, \tag{4}$$

where ρ_{min} and ρ_{max} is the apparent density of the initial (before swelling – frothing) granule and of the granule swelled to the maximal degree.

Formula (4) is the kinetic equation of pore formation under isothermal firing of granulated mineral material. In isothermal firing of granules within the temperature interval of 1123 – 1523 K, in which the principle variation (decrease) in the apparent density of granules made of different materials or mixtures takes place, the correlation coefficient is equal to 0.88 – 0.99. Furthermore, $b = 0.01 – 0.70$, which means substantial nonlinearity of the process of pore formation (swelling or frothing) in granules. Therefore, the measurement units of firing duration are very important. The experiments show that firing duration should be measured in minutes.

Let us now derive the kinetic equation for the pore formation in granules migrating inside the furnace (rotary furnace, tunnel kiln, etc.).

Let the apparent density of a granule within a certain time period vary between t and $t + \Delta t$ vary from $\rho(t)$ to $\rho(t + \Delta t)$; then equation (4) takes the following form:

$$\frac{1/[\rho(t+\Delta t)]-1/\rho_{min}}{1/\rho_{max}-1/\rho_{min}} = e^{-k\tau^b}. \qquad (5)$$

Since the value of Δt is low, by using decomposition in series, one can write:

$$e^{-k(\tau+\Delta t/60)^b} = e^{-k\tau^b(1+\Delta t/60)} = e^{-k\tau^b(1-kb\tau^{b-1}(\Delta t/60))}.$$

By substituting τ from expression (4) into expression (5) and performing certain transformations, we will get:

$$\frac{d(1/\rho)}{dt} = -\left(\frac{1}{\rho}-\frac{1}{\rho_{min}}\right)\left[\frac{1}{k}\ln\frac{1/\rho_{max}-1/\rho_{min}}{1/\rho-1/\rho_{min}}\right]^{1-1/b}.$$

But $dt = dl/v_m$; therefore, we finally obtain:

$$\frac{d(1/\rho)}{dt} = -\frac{kb}{60v_m} \times$$
$$\left[\left(\frac{1}{\rho}-\frac{1}{\rho_{min}}\right)\frac{1}{k}\ln\frac{1/\rho_{max}-1/\rho_{min}}{1/\rho-1/\rho_{min}}\right]^{1-1/b},$$

where v_m is the velocity of the progressive motion of granules in the furnace, m/sec; l is the furnace length, m.

The derivatographic analysis results and experimental data on swelling of argillaceous granules and frothing of granules made of glass powders of various chemical compositions indicate that the granule mass changes virtually only in the front zone of the furnace.

The mass of granules in isothermal heating varies in accordance with equation (3), in which the volume V is replaced by the granule mass m.

Similarly to the above equation, the equation of the granule mass variation under nonisothermal heating in a furnace takes the form:

$$\frac{dm}{dl} = -(m-m_{min})\frac{kb}{60v_m}\left[\frac{1}{k}\ln\frac{m_r-m_{min}}{m-m_{min}}\right]^{1-1/b}.$$

The kinetic equations of the pore-formation process in firing of granules can be used in mathematical modeling, in determination of the optimum parameters for firing granulated batches of mineral materials in various types of furnaces, and for designing automated systems to control the process parameters in the production of granulated foam glass and porous fillers.

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